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(71) Applicant
The Secretary of State for Defence
Whitehall, London, SW1A 2HB, United Kingdom

(72) Inventor
Ian Coulson

(74) Agent and/or Address for Service
R W Beckham
Procurement Executive Patents 1A(4),
Ministry of Defence,
Room 2014 Empress State Building, Lillie Road,
London, SW6 1TR, United Kingdom

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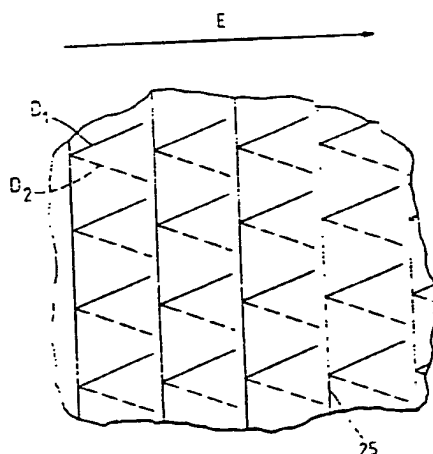
(52) UK CL (Edition J)
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(56) Documents cited by ISA
EP 0179592 A EP 0164814 A EP 0092181 A
FR 2567533 A
Applied Physics Letters, volume 47, no. 12,
15 December 1985 pages 1277-1279

(58) Field of search by ISA
INT CL^a C09K 19/00, G02F 1/00

(54) Liquid crystal devices

(57) A liquid crystal display device with a fast switching time and bistability comprises a layer of a chiral smectic material between cell walls. Electrodes on the walls allow the material to be switched between two states by application of positive and negative voltage pulses. Rapid switching is due to the ferro electric effect. Good alignment and uniformity of display is achieved by using an alignment giving a high, 5-45°, tilt to the liquid crystal molecules. Alignment may be provided by oblique evaporate of silicon monoxide at a glancing angle of up to 15°.



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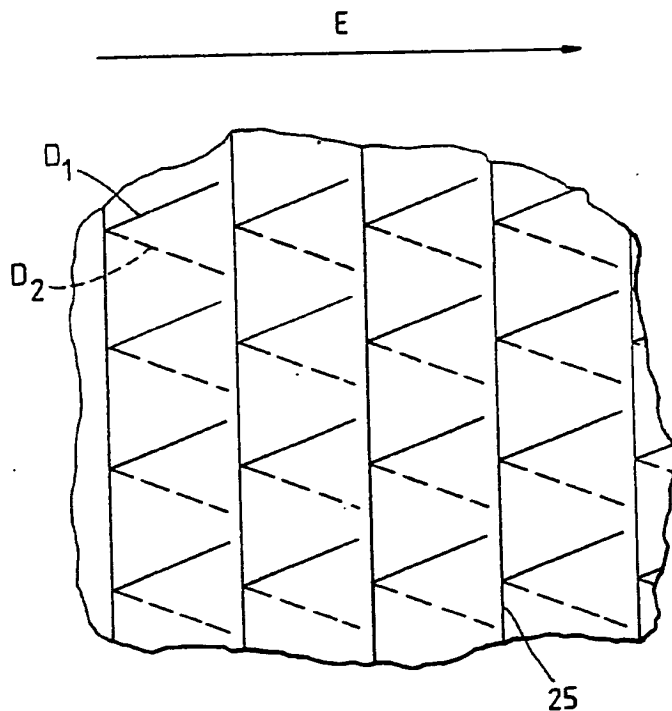
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<p>(21) International Application Number: PCT/GB87/00220</p> <p>(22) International Filing Date: 1 April 1987 (01.04.87)</p> <p>(31) Priority Application Number: 8608116</p> <p>(32) Priority Date: 3 April 1986 (03.04.86)</p> <p>(33) Priority Country: GB</p> <p>(71) Applicant (for all designated States except US): THE SECRETARY OF STATE FOR DEFENCE IN HER MAJESTY'S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND [GB/GB]; Whitehall, London SW1A 2HB (GB).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only) : COULSON, Ian [GB/GB]; 41a Dudley Gardens, Harrow, Middlesex HA2 ODQ (GB).</p>	<p>(74) Agent: BECKHAM, Robert, William; Procurement Executive, Ministry of Defence Patents 1A, Room 2014, Empress State Building, Lillie Road, London SW6 1TR (GB).</p> <p>(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB, GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), US.</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>	

(54) Title: LIQUID CRYSTAL DEVICES

(57) Abstract

A liquid crystal display device with a fast switching time and bistability comprises a layer of a chiral smectic material between cell walls. Electrodes on the walls allow the material to be switched between two states by application of positive and negative voltage pulses. Rapid switching is due to the ferro electric effect. Good alignment and uniformity of display is achieved by using an alignment giving a high, 5-45°, tilt to the liquid crystal molecules. Alignment may be provided by oblique evaporate of silicon monoxide at a glancing angle of up to 15°.



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LIQUID CRYSTAL DEVICES

The invention relates to smectic liquid crystal devices employing ferro electric smectic material.

5 Liquid crystal devices commonly comprise a thin layer of a liquid crystal material contained between two glass plates or walls. A thin transparent electrode is deposited on the inner face of both walls. The combination of liquid crystal layer, walls, and electrode is often termed a liquid crystal cell. When an electric field is applied between the two electrodes, liquid crystal
10 molecules rotate in the field to an ON state. On removal of the field the molecules rotate back to an OFF state, determined by a surface treatment applied to the walls before cell assembly and by the type of liquid crystal material. The optical transmission characteristics of the ON and OFF states are different. Some
15 devices need one or two polarisers and/or dyes to visibly distinguish between ON and OFF states.

There are broadly three different phases of liquid crystal material, nematic, cholesteric, and smectic, each distinguished by
20 a different molecular ordering.

Such materials only show a liquid crystal phase over a limited temperature range between the solid and isotropic liquid phases. Within the liquid crystal phase temperature range a material may
25 exhibit one or more of the nematic, cholesteric or smectic phase types. Normally a material is chosen such that it forms only one type of liquid crystal phase over its working temperature range.

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The present invention concerns devices using ferro-electric smectic liquid crystal materials.

5 Displays have been made with the electrodes formed into rows on one wall and columns on the other wall. These collectively form an x, y matrix of separately addressable elements on a large display. One way of addressing such a display is by multiplexing i.e. addressing each row in sequence until the whole display has been addressed. This is repeated all the time that a display is
10 needed. Another type of display uses the ON and OFF states to form an electrically switchable optical shutter. Yet another type of display is used as an optical storage device. Nematic cholesteric and smectic liquid crystal material have been used for such devices. A problem with many displays is the time taken to
15 switch between the two states i.e. the response times. For many displays a fast response time is needed. A nematic material, arranged in a 90° twisted structure typically has a response time of 100 milliseconds.

20 Devices comprising smectic materials have not been used as widely as devices with nematic or cholesteric materials. Available display devices based on smectic materials do not have the necessary characteristics. Recently however the smectic ferro-electric property with its fast switching and bistability
25 characteristics has become important see for example N. A. Clark & S. T. Lagerwall, App. Phys. Letters 36(11) 1980 pp 899-901.. Chiral materials in a tilted liquid crystal smectic phase, e.g. S_C^* , S_I^* , S_F^* , S_J^* , S_G^* S_H^* , are known to exhibit ferro-electric properties. This has been described by R. B. Meyer, L. Liebard,
30 L. Strzelecki, and P. Keller, J. de Physique (Lett.), 36, L-69 (1975).

- 3 -

A disadvantage of the devices using ferro-electric or chiral smectic (S*) materials is the non-uniformity of cells: they appear patchy. One particular kind of problem that arises in cells using a conventional alignment layer, such as a rubbed polyimide material as used in twisted nematic devices, is characterised by a "zig zag" defect, which is visible under microscopic examination and separates areas of the cell which exhibit different levels of contrast and angle of view. This produces an unacceptable visual appearance for a display or shutter using the smectic C material.

According to this invention the above problem is solved by using a cell wall surface treatment that gives a high tilt to contacting liquid crystal molecules.

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According to this invention a liquid crystal device comprises
two cell walls spaced apart by a spacer,
a layer of a chiral smectic liquid crystal material contained
between the walls,
5 electrode structures on the inner facing surfaces of the cell
walls,
a surface alignment coating on the inner facing surface of at
least one wall, the alignment coating providing both an
alignment direction and a surface tilt of above 5° to
10 contacting liquid crystal material
at least one polariser arranged with its optical axis parallel
to a liquid crystal molecular alignment direction,
and either an amount of a dichroic dye in the liquid crystal
material or a second polariser arranged so that the cell
15 walls are between both polarisers.

The alignment directions on the two walls may be parallel in the
same or opposite directions, although small variations are
acceptable.

20 A retarder may be incorporated between the polarisers to optimise
colour and contrast.

A reflector may be used and the device viewed in reflected light,
25 in which case the second polariser may be replaced by a retarder
between the cell and the reflector.

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The chiral smectic material has a cholesteric phase at a temperature above ambient between the smectic and isotropic phases. Preferably the cholesteric pitch p is greater than half the layer thickness d over a temperature range of 0.1°C or more above the smectic/cholesteric phase transition. The value of the spontaneous polarisation co-efficient P_s of the material is at least 0.1 and preferably 1 or more nC/cm^2 .

The liquid crystal material is heated into the isotropic phase and introduced between the walls by capillary action via two holes which are subsequently sealed, or by vacuum filling through a single hole. Once in place the liquid crystal material is heated into the cholesteric phase and slowly cooled to ambient temperature. This assists in obtaining good alignment and uniform appearance. A typical cooling rate is between 0.05 and 2°C/minute within $\pm 5^\circ\text{C}$ of the smectic/cholesteric phase transition.

Brief Description of the Drawings

One form of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:-

Figures 1, 2, are plan and section views of a liquid crystal display device;

Figure 3 is an enlarged view of part of Figure 1;

Figures 4a, b, c are graphs of cholesteric pitch against temperature for different materials.

Ambient temperatures may be taken as 0°C to 40°C for most displays. However for displays mounted on instruments or other equipment ambient operating temperature may reach 100°C .

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Description of Preferred Embodiment

- The cell 1 shown in Figures 1, 2, 3 comprises two glass walls 2, 3, spaced about 2-15 μm apart by a spacer ring 4 and/or distributed spacers. Electrode structures 5, 6 of transparent tin oxide are formed on the inner face of both walls. These electrodes may be of conventional row (x) and column (y) shape, radius and angle (r, θ) shape, or seven or more segment display for displaying alpha numerics. A layer 7 of smectic liquid crystal material is contained between the walls 2, 3 and spacer ring 4. Polarisers 8, 9 are arranged in front of and behind the cell 1. A d.c. voltage source 10 supplies power through control logic 11 to driver circuits 12, 13 connected to the electrode structures 5, 6, by lead wires 14, 15.
- The cell display may be observed by transmitted light, in which case a light source eg a tungsten bulb 16 is arranged behind the display. Alternatively a reflector 17 may be arranged behind the polarisers and the display observed by reflected light. Additionally a retarder (not shown) may be arranged between wall 3 and polariser 9.

Prior to assembly the walls 2, 3 coated with the electrodes 5, 6 are surface treated by the known process of oblique evaporation of silicon monoxide.

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This is described for example in G.B. 1,454,296, 1,472,247, 1,470,592. A stream of silicon monoxide is deposited onto a wall at an angle of up to 15° to the substrate surface. When used as described in the above specification with nematic liquid crystal materials this results in a uniform linear alignment of liquid crystal molecules and a tilt of 30° between the molecules and the wall. The alignment is analogous to rubbing which provides alignment of liquid crystal molecules but a tilt of about 2° . Different angles of molecular tilt may be produced by sequential evaporation of SiO at evaporation angles of up to 15° and angles between 15° and 30° . Varying the amounts of material deposited in these two directions varies the tilt angle between about 0° and 45° .

The smectic material is preferably one having a long pitch cholesteric phase above the smectic phase.

To provide a uniform alignment of both molecules 26 and micro-layers 25 it is necessary to use a smectic material with a cholesteric phase at elevated temperatures above device operating temperatures e.g. above 40°C or even 100°C depending on device use. Figure 4a shows a cholesteric pitch p versus temperature curve for a typical conventional smectic material with a cholesteric phase. As the temperature reduces very close to a cholesteric/smectic phase transition, pitch p increases towards infinity. Away from this transition cholesteric pitch becomes very small, typically much less than $1\text{ }\mu\text{m}$.

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Displays of the invention described in copending application numbers GB 86 08,114 and 86 08,115 filed together with the present invention have a long pitch in the cholesteric phase for at least 0.1°C above this phase transition. Preferably this range is 5°C and ideally occurs over the whole cholesteric temperature range. Within this range the minimum p is greater than $4d$, d being the layer thickness.

There are a number of ways of achieving the above material. For example combining one or more chiral components with laevo (left) cholesteric twist sense with one or more chiral components with dextro (right) cholesteric twist sense, with the proviso that none of the laevo components are the racemates of the dextro components. Such a mixture may be used by itself if it has the necessary smectic phases. Alternatively the chiral mixture may be added to a non-chiral or a racemate liquid crystal material, eg a smectic C host. Different chiral components may have different temperature/pitch characteristics. In this case it is necessary to ensure that the resultant pitch has the required value in the temperature range above the smectic/cholesteric phase transition.

When using chiral components of opposite twist sense it is necessary to ensure that the resultant mixture has the required spontaneous polarization value P_s . Thus all of the chiral components, regardless of their cholesteric twist sense, may have the same sense of S^* polarization, i.e. their P_s add. Alternatively one or more of the chiral components may have the opposite sense of P_s providing the net P_s has a sufficient value.

can add
non-chiral or
smectic C to
le y or
affecting
temp. pitch,
phase transition
characteristics

- 9 -

Another way of achieving the above material is to use one or more chiral components with the same cholesteric twist sense and S^* polarisation sense but still satisfying the cholesteric pitch values noted above. Such a mixture may be used alone or in combination with a non-chiral or a racemate liquid crystal material, eg a S_C host.

As a result of the long pitch in the cholesteric phase the material cools into the S_C^* phase with uniform alignment caused by the cell wall treatment. The result is alignment as in Figure 3.

The pitch in the smectic phase is arranged to be greater than about $1 \mu m$ and preferably very much greater.

The compensation of pitch in the cholesteric phase is illustrated in Figures 4(a), (b), (c). Figure 4(a) shows cholesteric pitch against temperature for a noncompensated material having a cholesteric to smectic transition. At this transition the pitch tends to infinity. The compensated material shown in Figure 4(b) shows a pitch increase a few degrees above the transition temperature with a pitch reduction below. By suitable selection of materials this pitch increase can be made to occur even closer to the transition temperature as in Figure 4(c), but a few degrees difference does not seem to affect the end result.

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- 10 -

When introduced into a cell liquid crystal molecules at the cell walls align along the evaporation direction of SiO marked E on Figure 3 with a surface tilt of eg 30°. The directions of E may be the same or in opposite directions on the two walls 2,3. Liquid crystal molecules are observed to adopt one of two alignment direction D1, D2 depending on the polarity of an applied voltage. A typical voltage is +/- 10 to 50 volts. These two positions are seen in Figure 3 in full D1 and broken lines D2, and lie either side of the evaporation/alignment direction E. Rapid switching between the two states, when the d.c. pulses are applied, is due to the smectic ferro electric property of the material. Typically the cell can be switched between D1 and D2 in times of a few μ s to a few ms eg 1ms depending on the liquid crystal material. The two different directions D1, D2 represent two different directions of Ps, often termed UP and DOWN directions. These two directions D1, D2 may be about 45° apart depending on the material composition.

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The polarisers 8, 9, Figures 1, 2, are arranged with their optical axes crossed. Polariser 8 is aligned with its axis parallel to direction D1. The cell 1 transmits light polarised in a plane parallel to the direction of molecular alignment D1 or D2. Thus in one state D1 of the cell very little light is passed through the combination of polariser 8, cell 1, and polariser 9.

However when the cell is in state D2 the molecules are at 45° to both polarisers 8, 9 optical axis and light is transmitted. Typical applied voltages are ± 15 to 20 volts for a $6\ \mu\text{m}$ thick layer of liquid crystal material, ± 5 to 10 volts for a $2\ \mu\text{m}$ thick layer, and \pm about 30 volts for a $12\ \mu\text{m}$ thick layer.

For the x, y matrix display of Figure 1 each electrode intersection x, y is addressed by a \pm voltage pulse; m, n are integers equal to the number of x and y electrodes respectively. These pulses switch the liquid crystal material at each x_m, y_n intersection to be light transmissive or opaque as required. Using a known technique of multiplex addressing each intersection is addressed in sequence. Such addressing may be an intersection at a time or a whole x row at a time.

Conventionally an x, y matrix needs to be continually refreshed, i.e. re-addressed, to maintain a flicker free display. The reason for this is that conventional nematic materials quite rapidly relax from one say ON state to say an OFF state. Conventional addressing refreshes each intersection before they have time to turn from ON to OFF. This imposes a severe limitation on the number of x, y intersections that can be addressed.

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In contrast cells of this invention possess true bistability. That is when switched into either D1 or D2 state they remain as switched for some seconds or even hours, depending on the cell material and construction, without any applied voltage until
 5 switched to the other state. This means that much larger numbers of intersections can be addressed without flicker of the display. Alternatively instead of refreshing the whole display only those parts to be changed are addressed.

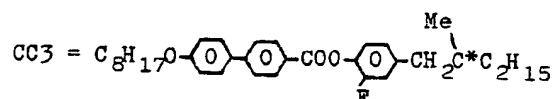
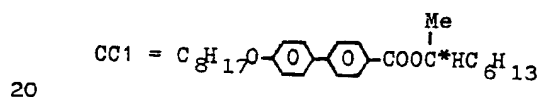
10 Materials suitable for use in cells of this invention are:-

Example 1

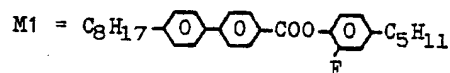
CM6 = 43.5% CD3 (chiral component) + 56.5% H1 (S host)

15

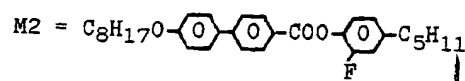
where CD3 = 22% CC1 + 78% CC3



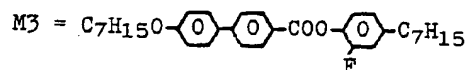
25 $H1 = M1 + M2 + M3 \quad (1:1:1)$



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- 13 -

CM6 has the following phases

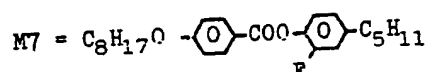
solid \rightleftharpoons chiral smectic \rightleftharpoons smectic A \rightleftharpoons cholesteric \rightleftharpoons isotropic

5 Example 2

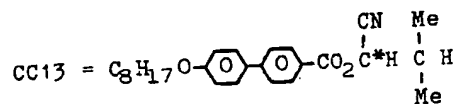
Merck ZLI 3041

10 Example 3

LPM13:- 72.5% H1 + 25% M7 + 2.5% CC13



15



20

LLM13 has the following phases:-

solid, chiral smectic 56.3° cholesteric 118° isotropic.

$$\text{Ps} = 10\text{nC/cm}^2 \text{ at } 20^\circ\text{C} \text{ and } 5\text{nC/cm}^2 \text{ at } 46^\circ\text{C}.$$

25

One example of a blue dye is D102 available from BDH Poole, Dorset, UK.

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Claims:-

1. A liquid crystal device comprising:-
two cell walls spaced apart by spacer,
a layer of a chiral smectic liquid crystal material contained
between the walls
5 electrode structures on the inner facing surfaces of the cell
walls,
a surface alignment coating on the inner facing surface of the
walls, the alignment coating providing both an alignment
direction and a surface tilt of above 5° to contacting
10 liquid crystal material
at least one polariser arranged with its optical axis parallel
to a liquid crystal molecular alignment direction,
and either an amount of a dichroic dye in the liquid crystal
material or a second polariser arranged so that the cell
15 walls are between both polarisers.
2. The device of claim 1 wherein the liquid crystal material
has a cholesteric phase at a temperature above ambient between the
smectic and isotropic phases.
20
3. The device of claim 2 wherein the liquid crystal material
has the following phases:
solid \rightleftharpoons chiral smectic \rightleftharpoons smectic A \rightleftharpoons cholesteric \rightleftharpoons isotropic.
25

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4. The device of claim 1 wherein the two alignment directions are parallel but opposite.
5. The device of claim 1 wherein the two alignment directions are parallel and in the same direction.
6. The device of claim 1 wherein the molecular tilt is in the range 10° to 45° .
7. The device of claim 1 wherein the two polarisers are arranged with their optical axis orthogonal.
8. The device of claim 1 wherein the liquid crystal material has a net spontaneous polarisation coefficient of greater than 0.1 nC/cm^2 .
9. The device of claim 1 wherein the liquid crystal material has a net spontaneous polarisation coefficient of greater than 1.0 nC/cm^2 .
10. The device of claim 2 wherein the liquid crystal material has a smectic phase over an operating temperature range up to 100°C .
11. The device of claim 2 wherein the liquid crystal material has a smectic phase over an operating temperature range up to 40°C .
12. The device of claim 1 wherein the layer of liquid crystal material is up to $15 \mu\text{m}$ thick.
13. The device of claim 1 wherein the electrodes are patterned into strip electrodes forming an x, y matrix array.
14. The device of claim 1 wherein the electrodes are patterned into strip electrodes forming an r, O matrix array.

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15. The device of claim 13 and further comprising driver circuits for addressing the matrix array.

16. The device of claim 1 wherein the electrodes are
5 patterned into segments for displaying numerical values.

17. The device of claim 1 wherein an at least partially reflecting mirror is arranged behind the device to reflect light back through the liquid crystal material and polariser.
10

18. The device of claim 1 and including a retarder plate.
11

1/3

Fig. 1.

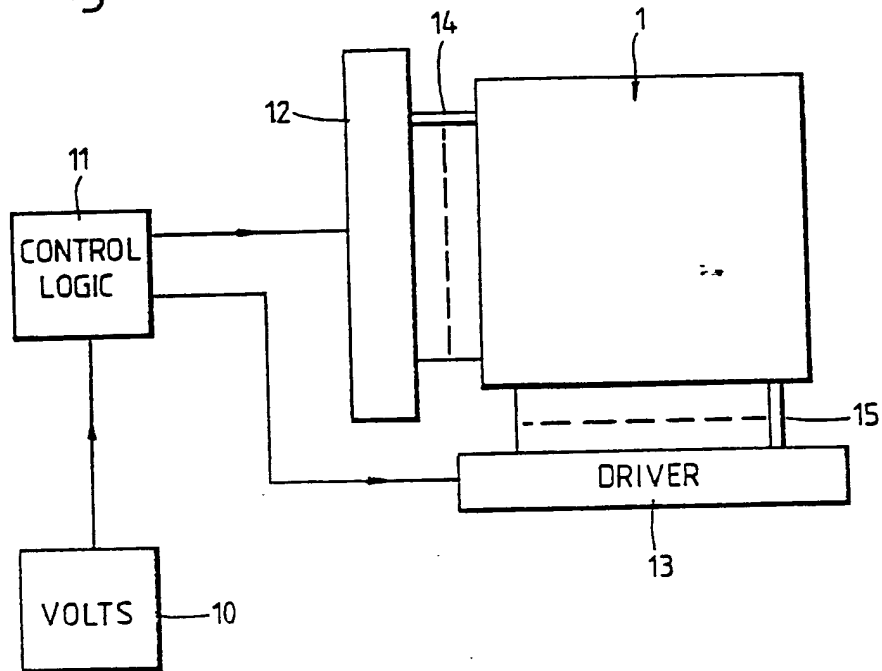


Fig. 2.

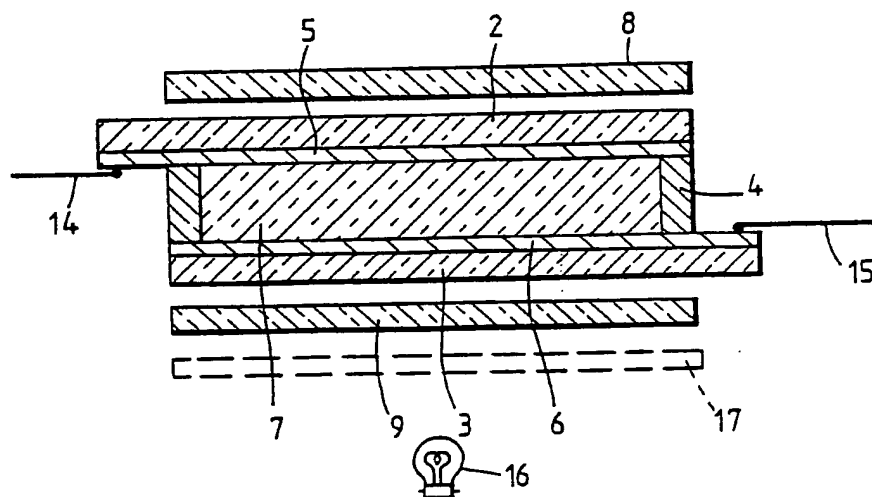


Fig. 3.

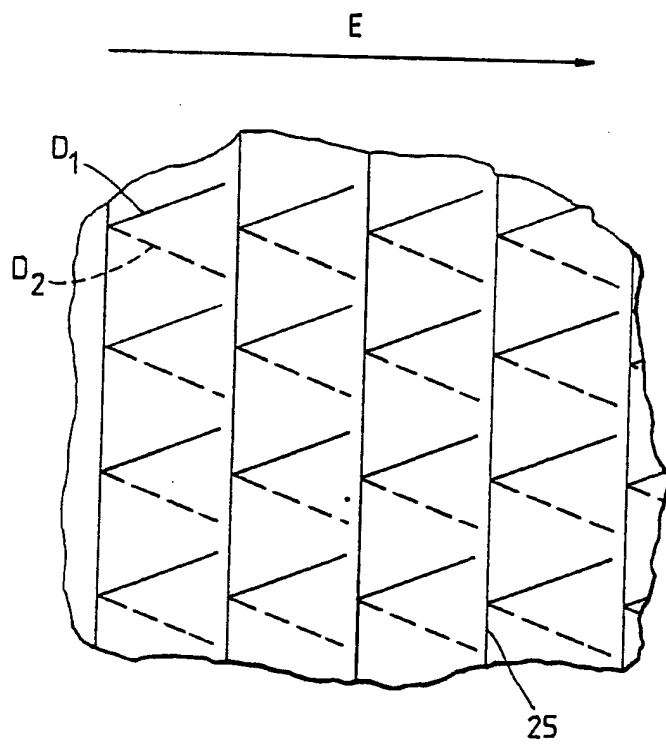


Fig.4a.

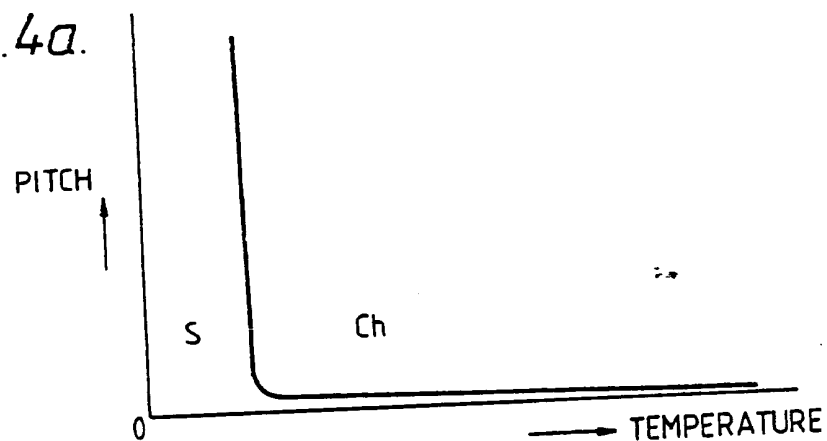


Fig.4b.

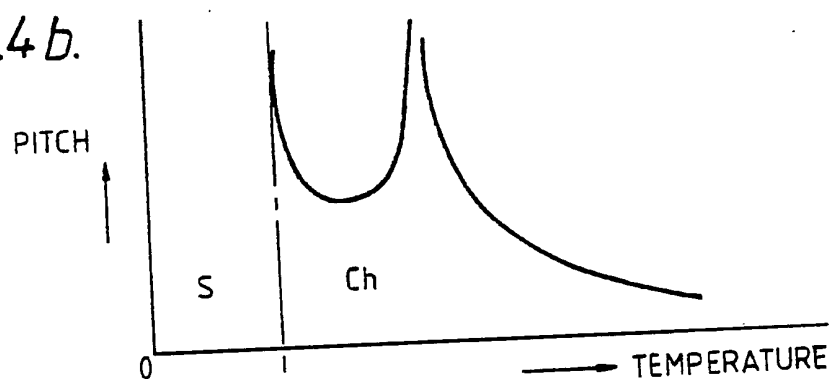
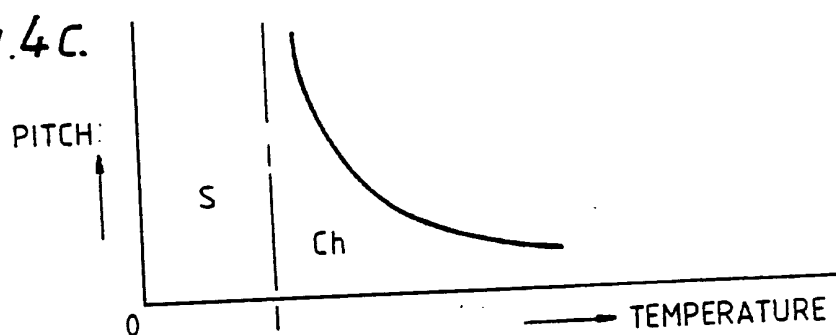


Fig.4c.



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 87/00220

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *
According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁴: G 02 F 1/137

II. FIELDS SEARCHED

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Classification Symbols
IPC⁴ | G 02 F 1/00; C 09 K 19/00

Documentation Searched other than Minimum Documentation
to the extent that such Documents are included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP, A, 0092181 (HITACHI, LTD) 26 October 1983	
Y	see page 6, line 20 - page 8, line 17	1,6,7,17 2,3,10,11, 13
Y	FR, A, 2567533 (CANON K.K.) 17 January 1986 see page 13, line 10 - page 10, line 8	2,3,10,11, 13
A	Applied Physics Letters, volum 47, no. 12, 15 December 1985, American Institute of Physics, (Woodbury, New York, US), J.S. Patel: "Room-temperature switching behavior of ferroelectric liquid crystals in thin cells", pages 1277-1279 see page 1278, left-hand column, lines 19-21	5
A	EP, A, 0164814 (CHISSO CORP.) 18 December 1985 see page 14, line 8 - page 16, line 18; page 11, table 4, sample no. 13-15; ./.	1-3,8,9

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IV. CERTIFICATION

Date of the Actual Completion of the International Search

4th July 1987

International Searching Authority

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Date of Mailing of this International Search Report

- 3 AUG 1987

Signature of Authorized Official
M. VAN MOL

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
P,X	pages 42-43, example 9 -- EP, A, 0179592 (DEUTSCHE ITT INDUSTRIES GmbH) 30 April 1986 see page 7, line 20 - page 9, line 12; page 10, line 13 - page 11, line 16; page 12, line 10 - page 13, line 8 -----	1-3,7,11

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO.

PCT/GB 87/00220 (SA 16659)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 16/07/87

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